MO 10: Posters 2: Biomolecules, Energy Transfer, Clusters, Quantum Chemistry, Molecular Dynamics and Chirality

Time: Tuesday 16:30–18:30 Location: Spree-Palais

MO 10.1 Tue 16:30 Spree-Palais

Polarization-resolved fluorescence-excitation spectroscopy of individual chlorosomes from the *bchR* - and *bchQR* - Mutant of Chlorobaculum tepidum — •Lisa Maria Wohlrab[1], Marc Jendrny[1], Donald A. Bryant[2], and Jürgen Köhler[1] — [1]Experimental Physics IV and Bayreuth Institute of Macromolecular Research (BIMF), Universität Bayreuth, Universitätsstr. 30, 95447 Bayreuth, Germany — [2]Department of Biochemistry & Molecular Biology, The Pennsylvania State University, 107 Althouse Lab, University Park, PA 16802

Chlorosomes are the main light-harvesting antennae complexes in green photosynthetic bacteria and contain bacteriochlorophyll *c*, *d* or *e* depending on the species. The chromophores self-assemble into aggregates without the involvement of a protein scaffold, and are organized in rods of 100 nm - 200 nm length and 20 nm - 50 nm width. For the species *Chlorobaculum tepidum* mutants (*bchR* and *bchQR*) have been prepared. The mutations affect the side groups of the BChl molecules.

Polarization resolved fluorescence-excitation spectroscopy on individual mutated chlorosomes reveal the importance of the methylation at $C-8^2$ position of the bacteriochlorophylls for the spectral properties of the chlorosomes.

MO 10.2 Tue 16:30 Spree-Palais

Broadband Microwave Spectroscopy of Biologically Relevant Complexes in the Gas Phase — •Sabrina Zinn[1,2,3], Thomas Betz[1,2,3], and Melanie Schnell[1,2,3] — [1]Max Planck Institute for the Structure and Dynamics of Matter, Hamburg/Germany — [2]Center for Free-Electron Laser Science, Hamburg/Germany — [3]The Hamburg Centre for Ultrafast Imaging, Hamburg/Germany

Molecular recognition plays an important role in nature and is often very sensitive to small changes in the geometric structure. To learn more about molecular recognition we want to study systems which mimic the cell recognition in the protein lectin, where the carbohydrates on a cell surface interact with the aromatic moieties of the protein. We want to study the importance of weak interactions, such as CH/π interactions, for this recognition process. Therefore we will focus on interactions between aromatic molecules such as tryptophan and monosaccharides such as glucose. In particular, we want to compare slightly different recognition partners to get information about the influence of functional groups, steric effects or the molecular forces, which are involved.

We use Chirped-Pulse Fourier-Transform Microwave spectroscopy (CP-FTMW) combined with a supersonic jet to study the molecular complexes. It allows us to record the rotational spectrum from 2 - 8.3 GHz within a single acquisition. We also implemented a laser-ablation source that is crucial for our studies on these fragile molecules.

MO 10.3 Tue 16:30 Spree-Palais

Single-Molecule Fluorescence-Excitation Spectroscopy on LH2 Complexes from *Allochromatium Vinosum* — •Alexander Löhner[1], Nichola Picken[2], Richard Cogdell[2], and Jürgen Köhler[1] — [1]Experimental Physics IV, University of Bayreuth, Germany — [2]Institute of Molecular, Cell & Systems Biology College of Medical Veterinary and Life Sciences, University of Glasgow, United Kingdom

The absorption spectrum of the high-light peripheral light-harvesting complex (LH2 complex) from the photosynthetic purple bacterium *Allochromatium vinosum* features two strong absorptions around 800 nm and 850 nm. In contrast to LH2 complexes from other species for the high-light LH2 complex from *Alc. Vinosum* the intruiging feature is that the B800 band is split into two components.

Fluorescence-excitation spectra of the B800 band from 71 single LH2 complexes have been registered. From that spectra it was possible to calculate the intra- and intercomplex spectral heterogeneity, and to extract the relative intensity and the homogeneous linewidth of the B800 absorptions. From this analysis and from the sum of the performed measurements we can rule out that the split of the B800 band comes from different types of LH2 complexes.

From comparison with computer simulations, we find the best agreement between simulation and experiment for a ring-like oligomer of 12 repeat units. The splitting of the B800 band can be reproduced if both an excitonic coupling between dimers of B800 molecules and their interaction with the B850 manifold is taken into account.

MO 10.4 Tue 16:30 Spree-Palais

Orientation dependence in S^{14+}+He_2 and S^{14+}+Ne_2 collisions at an impact energy of 11.37 MeV/u: Testing the impact parameter dependent ionization probabilities P(b) of S^{14+}+He and S^{14+}+Ne collisions. — •H. K. Kim[1], H. Gassert[1], J. N. Titze[1], M. Waitz[1], J. Voigtsberger[1], F. Trinter[1], J. Becht[1], A. Kalinin[1], N. Neumann[1], C. Zhou[2], L. Ph. H. Schmidt[1], O. Jagutzki[1], A. Czasch[1], M. Schöffler[1], H. Merabet[3], H. Schmidt-Böcking[1], T. Jahnke[1], H. J. Lüdde[1], A. Cassimi[2], and R. Dörner[1] — [1]University Frankfurt, Max-von-Laue-Str. 1, 60438 Frankfurt, Germany — [2]CIMAP Caen, Bd Henri Becquerel, BP 55027 * 14076 Caen Cedex 05, France — [3]Qatar University, P.O. Box: 2713 Doha, Qatar

We investigated the ionization of helium dimers (He_2) and neon dimers (Ne_2) by impact of very fast (11.37 MeV/u) S^{14+} projectile ions. We detect the Coulomb fragmenting ion pairs in the final charge states (He^{1+}+ He^{1+}) and (Ne^{n+}+ Ne^{m+}) with (n,m) := (1,1),(2,1),(3,1),(2,2). The events were detected in an ion-ion-electron coincidence with the COLTRIMS technique. The measured three dimensional momentum vectors allow to also access the energies and the direction in which the particles propagate. Multiple ionization shows a strong dependence on the orientation of the dimer axis with respect to the projectile beam axis. These orientation effects are attributed to the impact parameter dependent ionization probabilities P(b) for the atomic ionization processes S^{14+}+He and S^{14+}+Ne. By comparing the data to a Monte Carlo simulation we test these atomic P(b).

MO 10.5 Tue 16:30 Spree-Palais

Progress in imaging of ion molecule reactions — •Martin Stei, Eduardo Carrascosa, Alexander Dörfler, Aditya Kelkar, Thorsten Best, and Roland Wester — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck

Recent studies using our cross beam velocity map imaging (VMI) setup are presented. We have studied the reaction of F^- with CH_3Cl and have observed clear influence of the geometry of the transition state on the dynamics of the reaction, especially compared to our recent studies of the reactions of F^- and Cl^- with CH_3I [1,2]. We also report on our progress towards studying the influence of vibrational excitation of CH_3I on these reactions.

Furthermore we present the characterisation of three spatial map imaging modes of our 3D VMI spectrometer using multi-photon ionisation of toluene in a focused laser beam. A consistent analytical description of the imaging properties by a Taylor expansion has been applied and spatial resolution between 2 and 4 μm could be demonstrated [3].

[1] R. Wester, Phys. Chem. Chem. Phys. 16, 396 (2013) [2] J. Mikosch, J. Zhang, S. Trippel, C. Eichhorn, R. Otto, R. Sun, W. DeJong, M. Weidemüller, W. L. Hase, R. Wester, J. Am. Chem. Soc. 135, 4250 (2013) [3] M. Stei, J. von Vangerow, R. Otto, A. H. Kelkar, E. Carrascosa, T. Best, R. Wester, J. Chem. Phys. 138, 214201 (2013)

MO 10.6 Tue 16:30 Spree-Palais

Measurement of the Autoionization Lifetime of the Energetically Lowest Doubly-Excited $Q_1\,{}^1\Sigma_u^+$ State in H_2 using Electron Ejection Asymmetry — •Andreas Fischer[1], Alexander Sperl[1], Philipp Cörlin[1], Michael Schönwald[1], Sebastian Meuren[1], Joachim Ullrich[2], Thomas Pfeifer[1], Arne Senftleben[1], and Robert Moshammer[1] — [1]Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — [2]Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany

Dissociative single ionization of H_2 induced by broadband XUV photons has been studied in a kinematically complete experiment. Emphasis is put on the asymmetry in the electron emission direction with respect to the outgoing H^+-ion [1] as function of the excess- energies. The results are well reproduced by semi-classical model calculations that take into account interference effects along different dissociation pathways [2]. We further present a way to use the measured asymmetry to disentangle the two contributing interfering pathways, direct ionization and autoionization. From this we are able to determine the autoionization lifetime of the energetically lowest doubly-excited $Q1\,^1\Sigma_u^+(1)$ state for a large range of internuclear distances [3].

[1] Martín, F. et al. 2007 Science 315 5812
[2] Fischer, A. et al. 2013 PRL 110 213002
[3] Fischer, A. et al. 2013 J. Phys. B accepted

MO 10.7 Tue 16:30 Spree-Palais

Absolute configuration determination of a chiral epoxide using Coulomb Explosion Imaging — •Philipp Herwig[1], Kerstin Zawatzky[2], Manfred Grieser[1], Oded Heber[3], Brandon Jordon-Thaden[1], Claude Krantz[1], Oldřich Novotný[1,4], Roland Repnow[1], Volker Schurig[5], Dirk Schwalm[1,3], Zeev Vager[3], Andreas Wolf[1], Oliver Trapp[2], and Holger Kreckel[1] — [1]Max-Planck-Institut für Kernphysik, Heidelberg — [2]Organisch-Chemisches Institut, Ruprecht-Karls Universität Heidelberg — [3]Department of Particle Physics and Astrophysics, Weizmann Institute, Israel — [4]Columbia Astrophysics Laboratory, Columbia University, USA — [5]Institut für Organische Chemie, Eberhard Karls Universität Tübingen, Tübingen

Molecules that exist in two configurations, which are non-superimposable mirror images of one another, are called chiral. It is well known that the handedness of a chiral molecule influences its reactivity with other chiral species. Nevertheless, the assignment of absolute handedness still proves a challenging task. Here, we present the first successful experimental determination of the absolute configuration of selected enantiomers in the gas phase, using foil-induced Coulomb Explosion Imaging [1]. Fast oxirane molecules were passed through a thin stripping foil, where the binding electrons are removed in sub-femtoseconds, causing the charged nuclei to repel each other strongly. The relative fragment velocities for individual molecular breakups were recorded and reveal the handedness of the molecules.
[1] Herwig et al., Science, Vol. 342, 1084-1086, 2013

MO 10.8 Tue 16:30 Spree-Palais

Imaging the structure of pure and isotopic helium trimers — •Jörg Voigtsberger[1], Stefan Zeller[1], Jasper Becht[1], Nadine Neumann[1], Felix Sturm[1,2], Maksim Kunitski[1], Anton Kalinin[1], Jian Wu[1,3], Markus Schöffler[1], Wieland Schöllkopf[4], Dario Bressanini[5], Achim Czasch[1], Klaus Ullmann-Pfleger[1], Lothar Ph. H. Schmidt[1], Robert Grisenti[1], Till Jahnke[1], and Reinhard Dörner[1] — [1]Universität Frankfurt a.M., Institut für Kernphysik, Frankfurt, Germany — [2]Lawrence Berkeley National Laboratory, Chemical Sciences Division, Berkeley, USA — [3]East China Normal University, State Key Lab of Precision Spectroscopy, Shanghai, China — [4]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Dep. of Mol. Phys., Atom and Molecule Optics, Berlin, Germany — [5]University of Insubria, Department of Chemical and Environmental Sciences, Corno, Italy

We were able to measure the structure of $^4He_3$ and $^4He_2{}^3He$ by ionizing a jet of trimer clusters with a femtosecond Ti:Sa Laser. After expanding the gas through a precooled $5\mu m$ nozzle, clusters of different mass were separated by a transmission diffraction grating. Ionization with a strong laser field led to a coulomb explosion of the trimer. In a ColTRIMS apparatus the 3d momenta of all ionized fragments were measured, giving a direct access to the structure of the trimer. Results are compared to recent theory.

MO 10.9 Tue 16:30 Spree-Palais

Experimental observation of the vibrational wavefunction of helium dimers using strong laser-fields — Jörg Voigtsberger[1], •Stefan Zeller[1], Jasper Becht[1], Nadine Neumann[1], Felix Sturm[1,2], Maksim Kunitski[1], Anton Kalinin[1], Jian Wu[1,3], Markus Schöffler[1], Wieland Schöllkopf[4], Achim Czasch[1], Lothar Ph. H. Schmidt[1], Robert Grisenti[1], Till Jahnke[1], and Reinhard Dörner[1] — [1]Goethe Universität Frankfurt a.M., Institut für Kernphysik, Frankfurt, Germany — [2]Lawrence Berkeley National Laboratory, Chemical Sciences Division, Berkeley, USA — [3]East China Normal University, State Key Lab of Precision Spectroscopy, Shanghai, China — [4]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Dep. of Mol. Phys., Atom and Molecule Optics, Berlin, Germany

Helium gas is being expanded through a pre-cooled 5 μm nozzle in a supersonic gas jet at low temperatures. Containing small clusters this gas jet passes a transmission diffraction grating, separating clusters of different masses. The first order dimer diffraction peak is overlapped with a femtosecond Ti:Sa Laser and ionised. The Coulomb exploding ionic fragments are measured with the COLTRIMS technique, giving direct access to the square of the vibrational wavefunction. The enormous size and the small binding energy can be directly accessed via this approach.

MO 10.10 Tue 16:30 Spree-Palais

Electrophilic and Nucleophilic Oxygen in Cationic Gold-Oxygen Cluster Complexes — •Alexander P. Woodham and André Fielicke — Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany

Clusters, small aggregates of atoms or molecules, exhibit properties which are often unique and unlike those of either the bulk material or the atom. One of the most well-known examples is that of gold clusters which, in contrast to the highly inert bulk phase, play part in a range of oxidation reactions utilizing molecular oxygen as a feedstock. The origin for this change in reactivity is poorly understood and better characterization of the gold cluster complexes with oxygen may reveal structural or mechanistic details. Recent work has focused on the anionic and neutral clusters as the cationic clusters are thought to be unreactive towards molecular oxygen. In this poster, however, we present data for the binding and activation of molecular oxygen by cationic gold clusters. Spectroscopic characterization from infrared multiple photon dissociation spectroscopy (IR-MPD) allows determination of the oxidation state of bound oxygen molecules and unequivocally identifies the presence of both electron rich and electron poor adsorbates, even within the same cluster-complex composition.

MO 10.11 Tue 16:30 Spree-Palais

Vibrationally resolved fluorescence spectra of higher diamondoids — •Andrea Merli[1], Robert Richter[1], Christoph Heidrich[1], Ramon Rahner[1], Torbjörn Rander[1], Jeremy Dahl[2], Robert Carlson[2], Jens Petersen[3], Merle Röhr[3], Roland Mitric[3], and Thomas Möller[1] — [1]Institut für Optik und Atomare Physik,Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany — [2]Stanford Institut for Materials and Energy Science, Stanford University, California, 94305, USA — [3]Institut für Physikalische und Theoretische Chemie, Julius-Maximilians Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Size and shape selected pristine diamondoids are optimal interaction-free systems for the investigation of electronic properties of molecular clusters in the gas phase. Vibrationally resolved emission spectra were obtained by exciting higher diamondoids with narrow band ultraviolet laser light. The origin of the spectra is found to be on transitions from the first electronically excited state into different vibrational modes of the electronic ground state. Quantum chemical calculations offer an accurate vibrational analysis of the diamondoids spectra making the assignment of the optically active normal modes possible.

MO 10.12 Tue 16:30 Spree-Palais

Characterizing the binding mechanisms of metal cluster-diamondoid hybrids — •Tobias Zimmermann[1], Andre Knecht[1], Robert Richter[1], Andrea Merli[1], Konstantin Hirsch[2], Tobias Lau[2], Thomas Möller[1], and Torbjörn Rander[1] — [1]Technische Universität Berlin, Berlin, Deutschland — [2]Helmholtz-Zentrum für Materialien und Energie, Berlin, Deutschland

Metal cluster-diamondoid hybrid systems are expected to give new opportunities for studying electronic coupling mechanisms in tailor made nano scale semi-conductor systems. Diamondoids on one hand show shape and size dependent optical properties. Together with metal clusters which are mass selectable down to a size regime where every atom counts, they yield a broad range of parameters with which the electronic structure of the resulting hybrid system can be modified. First theoretical investigations hint at resonance effects for the optical and UV absorption region.

In this proof-of-principle study, we synthesized metal cluster-diamondoid hybrid systems and identified influences on the reactivity of metal clusters with (functionalized) diamondoids. Initial results, details of the experimental set-up and future extensions will be presented.

MO 10.13 Tue 16:30 Spree-Palais

IR and VIS spectroscopy on isolated ionic cobalt(ethanol) and nickel(ethanol) clusters — •Markus Becherer[1], Tobias C. Martin[1], Adam Kubas[2], Wei Jin[3], Georg Lefkidis[3], Karin Fink[2], Wolfgang Hübner[3], and Markus Gerhards[1] — [1]TU Kaiserslautern, Fachbereich Chemie, 67663 Kaiserslautern — [2]Karlsruher Inst. Technol., Inst. Nanotechnol., 76021 Karlsruhe — [3]TU Kaiserslautern, Fachbereich Physik, 67663 Kaiserslautern

Investigations on clusters containing transition metals and aliphatic ligands provide the opportunity to study the differences between small molecular systems and nanoscaled particles. The successive aggregation of ligands (e.g. alcohol molecules) and their adsorption products on nickel-dimer-clusters are investigated in a molecular beam experiment. To obtain structural information about the (nickel)$_2$(ethanol)$_{1-3}$ cluster-cations and the (nickel)$_2$(ethanol)$_1$ anion the frequencies of the OH-stretching vibrations are probed by means of IR-photofragmentation spectroscopy. The structural assignment is performed by comparing the experimental data with calculated frequencies obtained from DFT calculations. The results give insight into both, the structure and reactivity of the nickel aggregates. In case of the isolated cationic (cobalt)$_3$(ethanol)$_1$ and (cobalt)$_3$(ethanol)$_1$(water)$_1$ clusters IR spectra as well as electronic spectra in the VIS region are investigated by applying photodissociation spectroscopy. The experimentally observed spectra serve as probe for theoretical calculations especially on the electronic transitions within the triangular Co trimer metal centre.

MO 10.14 Tue 16:30 Spree-Palais

Structural investigations on isolated 7-hydroxy-4-methylcoumarin aggregates in different electronic states by combined IR/UV spectroscopy — •Anke Stamm, Martin Weiler, Kirsten Schwing, and Markus Gerhards — Physikalische Chemie, TU Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern

Coumarin and its derivatives are well known for their photo-induced reactivity leading to their importance as photobiological and photochemical substances. 7-Hydroxy-4-methylcoumarin (7H4MC) for example was the first industrially used optical brightener. Thus the structural analysis of such photoreactive substances is of high scientific interest. For this purpose the application of combined double and triple resonance IR/UV methods in a molecular beam experiment is performed. These experimental techniques in combination with DFT calculations represent and ideal tool to investigate intrinsic structural preferences and rearrangements in the neutral electronic ground (S_0), excited state (S_1) as well as in the ionic ground state (D_0). The focus of the results presented here is on the tetra-, penta- and hexahydrate of 7H4MC which are of importance regarding the influence of a biologically relevant solvent shell on the photochemical behavior. Additionally, studies on the dimer of 7H4MC as well as its mono- and dihydrate are illustrated.

MO 10.15 Tue 16:30 Spree-Palais

Hidden charge states in soft xray laser produced nanoplasmas revealed by fluorescence spectroscopy — •A. Przystawik[1], L. Schrödter[1], M. Müller[2], A. Kickermann[1], S. Toleikis[1], M. Adolph[2], L. Flückinger[2], T. Ghorkover[2], L. Nösel[2], M. Krikunova[2], T. Oelze[2], Y. Ovcharenko[2], D. Rupp[2], M. Sauppe[2], D. Wolter[2], S. Schorb[3], C. Bostedt[3], T. Möller[2], and T. Laarmann[1] — [1]DESY Hamburg, Germany — [2]TU Berlin, Germany — [3]SLAC, Stanford, USA

Highly charged ions are formed in the center of composite clusters by strong free-electron laser pulses and they emit fluorescence on a femtosecond time scale before competing recombination leads to neutralization of the nanoplasma core. In contrast to mass spectrometry that detects remnants of the interaction, fluorescence in the extreme ultraviolet spectral range provides fingerprints of transient states of high energy density matter. Spectra from clusters consisting of a xenon core and a surrounding argon shell show that a small fraction of the fluorescence signal comes from multiply charged xenon ions in the cluster core. Initially, these ions are as highly charged as the ions in the outer shells of pure xenon clusters with charge states up to at least 11+.

MO 10.16 Tue 16:30 Spree-Palais

Gas Phase Vibrational Spectroscopy of Messenger-tagged Aluminum Oxide Clusters Anions — •Matias R. Fagiani[1], Xiaowei Song[1], Wieland Schöllkopf[1], Sandy Gewinner[1], Florian A. Bischoff[2], Joachim Sauer[2], and Knut R. Asmis[1,3] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — [2]Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, D-12489 Berlin, Germany — [3]Wilhelm-Ostwald-Institut, Universität Leipzig, Linnéstr. 2, D-04103 Leipzig, Germany

Alumina structures of reduced dimensionality are of interest in astrophysics and atmospheric chemistry, as well as in nanostructured ceramic materials and solid catalysts. Little is known, experimentally, concerning the geometric structure of such clusters. Vibrational spectroscopy combined with electronic structure calculations provides more detailed insight into the geometric and electronic structure of these clusters.

Here, we present infrared photodissociation (IRPD) spectra of aluminum oxide cluster anions, focusing mainly on the fully-oxidized, electronic closed-shell clusters. The cluster anions are formed in a sputtering source. Mass-selected anions are trapped, cooled to cryogenic temperatures and messenger-tagged (D_2) in a buffer gas filled ion trap. Photodissociation spectra are measured from 400 to 1200 cm^{-1} with the widely tunable IR radiation of the free electron laser FHI FEL. The spectra are assigned and cluster structures are determined by comparison with the results of density functional calculations.

MO 10.17 Tue 16:30 Spree-Palais

New Setup for Core-Level PES on free mass selected Metal Clusters — •Michael Köther[1], Patrice Oelssner[1], Jens Bahn[1], Volkmar Senz[2], Christian Braun[3], Steffen Palutke[4], Bernd von Issendorff[5], Eckhart Rühl[6], Gerd Ganteför[3], Dieter Bauer[1], Josef Tiggesbäumker[1], and Karl-Heinz Meiwes-Broer[1] — [1]Inst. für Physik Universität Rostock — [2]Inst. für Biomed. Technik Universität Rostock — [3]FB Physik Universität Konstanz — [4]Inst. für Physik Universität Hamburg — [5]Fak. für Physik Universität Freiburg — [6]Physik und theoretische Chemie FU Berlin

Previous experiments at the FEL (FLASH) in Hamburg have shown distinct changes in the binding energy of core level electrons with respect to the cluster sizes. With higher photon energies available it is now possible to excite even deeper core electrons. On the other hand higher target densities are necessary to do qualitative research. We want to introduce a new setup for Core-Level PES utilizing a helium cooled RF-Trap for maximum target density and energy resolution.

The project is part of the Collaborative Research Center (SFB) 652.

MO 10.18 Tue 16:30 Spree-Palais

A Relativistic Time-Dependent Density Functional study of the excited states for the mercury dimer. — •Ossama Kullie — Institute for Physics, Department for Mathematics and Natural Science, Uni Kassel. And Institute de Quantique Chimie, Uni Strasbourg, France.

In this work [1] I present a time-dependent density functional (TDDFT) study for the ground-state as well as the excited states corresponding to the $(6s^2 + 6s6p)$, $(6s^2 + 6s7s)$ and $(6s^2 + 6s7p)$ atomic asymptotes for the mercury dimer Hg2. We analyze its spectrum obtained from all-electron calculations performed with the relativistic Dirac-Coulomb and relativistic spinfree Hamiltonian as implemented in Dirac-Package. Our result is excellent for the most of the lower excited states and very encouraging for the higher excited states, it shows generally good agreements with experimental results and outperforms other theoretical results. This enables us to give a detailed analysis of the spectrum of Hg2 especially for the relativistic effects, the spin-orbit interaction, and the performance of CAMB3LYP functional approximation and is enlightened for similar systems. [1] submitted to the J. chem. phys. 2013.

MO 10.19 Tue 16:30 Spree-Palais

Multiple time scale population transfer-dynamics in coupled electronic states — Martin Kess, Christoph Brüning, and •Volker Engel — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg, Germany

We regard the wave-packet dynamics in two electronic states which interact via a constant coupling element. Performing numerical calculations it is found that the time-dependent populations exhibit oscillatory variations with two characteristic periods. Whereas, as expected, one period is determined by the vibrational motion, it is shown that Rabi-type oscillations occur which are influenced by the parameters of the potential energy curves, the coupling and the amplitudes in the two states on one hand, and by the nuclear motion on the other. An analysis of the numerical results is performed within various levels of approximation.

Furthermore, we investigate how these structures survive if the one-dimensional model is extended to more degrees of freedom.

MO 10.20 Tue 16:30 Spree-Palais

Carrier Envelope Phase Effects induced by weak multicycle pulses: localized quantum dynamics in double well potentials

— •Kilian Hader[1,2], Klaus Renziehausen[1,2], and Volker Engel[1,2] — [1]Institut für Physikalische und Theoretische Chemie, Uni Würzburg — [2]Campus Nord, Am Hubland, Emil-Fischer-Str. 42, 97074 Würzburg, Germany

We study the laser-driven quantum dynamics in a double well potential. Within a two-pulse excitation scheme the first pulse prepares a linear combination of excited states with ungerade symmetry. The interaction with a second uncorrelated pulse of low intensity results in coherent superpositions of states with gerade and ungerade symmetry. This is associated with a localization of excited state wave packets. It is shown that the carrier envelope phase of the second laser pulse critically influences this time-dependent localization.

MO 10.21 Tue 16:30 Spree-Palais

Stochastic wave-function approach to two-dimensional vibronic spectroscopy

— •Johannes Wehner[1], Mirjam Falge[1], Walter T. Strunz[2], and Volker Engel[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg, Germany — [2]Institut für Theoretische Physik, TU Dresden, 01062 Dresden, Germany

Wave-packet dynamics derived from the time-dependent Schrödinger equation is nicely illustrative because it appeals to our classical intuition. However, there is no single reduced wave-packet for a system interacting with an environment. Nevertheless, the wave packet picture for the system dynamics can still be used under certain assumptions concerning the system-bath coupling. If the reduced density matrix fulfills a master equation of the Lindblad type, stochastic wave function equations can be set up which, in the average, are equivalent to the Lindblad master equation. We apply the quantum-diffusion stochastic approach to two-dimensional vibronic spectroscopy. Spectra are calculated and related to the underlying stochastic wave-packet dynamics.

MO 10.22 Tue 16:30 Spree-Palais

The time-scale of nonlinear events driven by strong fields: Can one control the spin-coupling before ionization runs over?

— •Mirjam Falge[1], Patricia Vindel-Zandbergen[2], Volker Engel[1], Manfred Lein[3], Bo Y. Chang[4], and Ignacio R. Sola[2] — [1]Universität Würzburg, Institut für Physikalische und Theoretische Chemie, Campus Nord, Emil-Fischer-Str. 42, 97074 Würzburg, Germany — [2]Departamento de Quimica Fisica, Universidad Complutense, 28040 Madrid, Spain — [3]Leibniz Universität Hannover, Institut für Theoretische Physik, Appelstraße 2, 30167 Hannover — [4]School of Chemistry (BK21), Seoul National University, Seoul 151-747, Republic of Korea

An initially populated spin manifold interacting with an external field can decay via spin-coupling or via ionization. Using a simple two-level Hamiltonian we investigate the relation between spin coupling and ionization rate and identify conditions for an efficient spin-control by suppressing ionization. The results are confirmed in solving the time-dependent Schrödinger equation for the interaction of a laser field with a spin-coupled model system where two electrons and a nucleus move in a collinear configuration. It is thus shown, that quantum control of intersystem crossing can indeed be effective if the intensity of the external field and the accompanying Stark-shift is adjusted properly to the spin coupling-strength.

MO 10.23 Tue 16:30 Spree-Palais

Laser-Driven Wave Packet Dynamics of Metal-Dicarbonyls

— •Mateusz Lisaj and Oliver Kühn — Institute of Physics, University of Rostock, Rostock, Germany

Metal-carbonyls play important roles in physiological and catalytic processes. In this contribution we aim at obtaining fundamental insight into the interactions responsible for bond dissociation by applying shaped laser pulses to steer molecular quantum dynamics. Specifically, $CpCo(CO)_2$ is studied on the basis of a four-dimensional reactive potential energy surfaces, containing the two carbonyl vibrations as well as the respective metal-carbonyl bond dissociation coordinates. Potential end dipole moment surfaces are obtained using density functional theory with the B3LYP functional and the LanL2DZ basis set. The time-dependent Schrödinger equation is solved employing the multi-configuration time-dependent Hartree method. Laser pulse optimization is performed with the goal to transfer as much energy as possible from the initially excited carbonyl vibration onto the metal-carbonyl bond such as to trigger bond breaking.

MO 10.24 Tue 16:30 Spree-Palais

Photoelectron Circular Dichroism of Chiral Molecules from Multiphoton Ionization with Femtosecond Laser Pulses: Intensity and Ellipticity studies

— Christian Lux[1], •Stefanie Züllighoven[1], Cristian Sarpe[1], Matthias Wollenhaupt[2], and Thomas Baumert[1] — [1]Universität Kassel, Institut für Physik und CINSaT, D–34132 Kassel, Germany — [2]Carl von Ossietzky Universität Oldenburg, Institut für Physik, D–26129 Oldenburg, Germany

Photoelectron Circular Dichroism (PECD) - i.e. the difference of the Photoelectron Angular Distribution (PAD) from ionization with left circularly polarized light and the PAD from ionization with right circularly polarized light - shows asymmetries in the electron emission from chiral enantiomers relative to the light propagation direction and was so far investigated using synchrotron radiation [1]. The magnitude of PECD is several orders larger than typically chirooptical asymmetries. We have demonstrated that PECD on randomly oriented chiral enantiomers is accessible via a 2+1 REMPI (Resonance Enhanced Multi-Photon Ionization) using femtosecond laser pulses. We detected highly structured asymmetries in the ±10% regime [2]. In this contribution we present our recent findings on the bicyclic Ketones Camphor, Norcamphor and Fenchone. From the results on variation of the laser intensity, we conclude an underlying dissociative ionization. The PECD can be unambiguously attributed to direct ionization of the parent ion. Ellipticity studies show the robustness of the PECD effect.

[1] I. Powis in S. A. Rice (Ed.): Adv. Chem. Phys. **138**, 267-329 (2008)

[2] C. Lux et al., Angew. Chem. Int. Ed. **51**, 5001-5005 (2012)

MO 10.25 Tue 16:30 Spree-Palais

Twin Mass Peak Ion Source for Determination of Chiral Enantiomers with Femtosecond Laser Pulses

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In the recent past, a specific anisotropy was observed in the gas phase ionization of chiral enantiomers using circularly polarized laser pulses [1,2]. The implementation of a twin mass peak ion source enabled the direct determination of this anisotropy applying nanosecond laser pulses [1]: A focused circularly polarized laser beam passes a second lens, is back-reflected via a mirror and with changed helicity again focussed into the time-of-flight mass spectrometer. A small spatial displacement of both foci results in time-separated mass spectra. Fluctuations in the shot-to-shot laser pulse energy, the gas density or the ion detection can be circumvented. However, this technique is not suitable for femtosecond laser pulses which are strongly affected by optical dispersion. In this contribution we discuss the current status of an in-line optical setup applicable for femtosecond laser pulses.

[1] C. Logé, U. Boesl, Chem. Phys. Chem. **12**, 1940-1947 (2011)

[2] P. Horsch, G. Urbasch, K.-M. Weitzel, Chirality **24**, 684-690 (2012)

MO 10.26 Tue 16:30 Spree-Palais

PEGASUS: Building an intense spin-polarized electron gun - status report

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The PEGASUS project aims at building an intense and portable spin-polarized electron gun for experiments in crossed beams arrangements at various ion beam facilities. The electron beam will cover energies between 1 and 10 keV at electron currents up to 100 μA. As source material we will utilize laser-induced electron emission from GaAs photocathodes which will be prepared in a state of negative electron affinity. With a set of electrostatic lenses and benders, the electrons will be transported to the interaction zone and Wien-filters will be used for controlling the spin orientation.

We give a status report on our progress for building the setup and discuss foreseen experiments.

MO 10.27 Tue 16:30 Spree-Palais

Direkte Bestimmung der stereochemischen Absolutkonfiguration mittels Coulomb-Explosion-Imaging

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Die Untersuchung molekularer Chiralität ist von weitreichendem Interesse in der Chemie und Biologie, aber auch für fundamentale Fragen wie die Paritätsverletzung. Trotz zahlreicher experimenteller Ansätze ist die Bestimmung der absoluten Konfiguration, d.h. der mikroskopischen Händigkeit, nach wie vor für viele flüssige und gasförmige Substanzen nur indirekt möglich. Wir zeigen unsere kürzlich veröffentlichten Ergebnisse [1], in denen es gelungen ist, die absolute Konfiguration der chiralen Methanderivate CHBrClF und CHBr^{35}Cl^{37}Cl mittels Coulomb Explosion Imaging (CEI) zu bestimmen. Mithilfe der Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) war es möglich, für individuelle Moleküle die Händigkeit zu ermitteln. Diese Strukturinformation kann nun mit Photo-Elektron-Spektra kombiniert werden, um so ein detaillierteres Verständnis des Photo-Elektronen-Dichroismus (PECD) zu erhalten.

[1] M.Pitzer et al., Science Vol. 341, p.1096 (2013)

MO 10.28 Tue 16:30 Spree-Palais

Chiralitätsbestimmung einfacher organischer Moleküle mittels Coulomb Explosion Imaging — •Kristina Zerbe, Martin Pitzer, Maksim Kunitski, Lothar Ph. H. Schmidt, Gregor Kastirke, Markus S. Schöffler, Horst Schmidt-Böcking und Reinhard Dörner — Institut für Kernphysik, Goethe-Universität Frankfurt am Main

Chiralität ist eine wichtige Eigenschaft von Molekülen, die in Physik, Chemie und Biochemie von großer Bedeutung ist. Die Bestimmung der absoluten Konfiguration, also der räumlichen Anordnung der Atome oder Atomgruppen um ein chirales Zentrum, ist bislang nur für kristallisierbare Stoffe mittels anomaler Röntgenbeugung möglich.

Unsere Gruppe [1] hat mittels Coulomb Explosion Imaging (CEI) und Cold Target Recoil Ion Moment Spectroscopy (COLTRIMS) bereits die absolute Konfiguration von Brom-Chlor-Fluormethan und weiteren Methanderivaten bestimmen können. Aufbauend darauf soll dies nun für größere gasförmige Moleküle (mehr als ein Kohlenstoffatom) erweitert werden. Die nun folgenden Untersuchungen des Fragmentierungsverhaltens von 2-Hydroxypropansäure und 2-Brompropansäure in Abhängigkeit von der Laserintensität, -pulslänge und -polarisation sollen vorgestellt werden.

[1] M. Pitzer et al., Science Vol. 341, p.1096 (2013)